DOI 10.1007/s10717-014-9646-6
*Glass and Ceramics*, Vol. 71, Nos. 5 – 6, September, 2014 (Russian Original, Nos. 5 – 6, May – June, 2014)

# SCIENCE FOR CERAMIC PRODUCTION

UDC 666.76

## INVESTIGATION OF HIGH-TEMPERATURE CREEP IN MULLITE – ZIRCONIUM OXIDE POLYDISPERSE CERAMIC

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Translated from *Steklo i Keramika*, No. 5, pp. 36 – 40, May, 2014.

The behavior of ceramic samples, based on mullite modified by zirconium oxide, during bending at high temperatures is investigated. It is shown that recrystallization annealing can be recommended to improve the properties of this material.

***Key words:*** superplasticity, mullite, zirconium oxide, high-temperature strength.

The rapid development of new technology, including aerospace technology, over the last few decades has made it necessary to develop relatively low-density materials capable of operating reliably at high temperatures in oxidizing media [1]. Two types of ceramic materials are being developed to solve this problem: oxygen-free ceramics and composites, based on silicon carbide and nitride and carbon, and oxide ceramic materials with diverse structure, containing corundum and mullite as the main phases [2, 3]. During the first few phases of the development of such materials more attention was devoted to oxygen-free ceramic and composite materials based on them, having very good mechanical properties and high working temperatures [4].

But, the inadequate resistance to oxidation and the damage to the protective coatings that were found in the course of the investigations [5, 6] and operation [7] of such materials led to the resumption of work on increasing the reliability of oxygen-free and low-oxygen materials and to the revival of interest in oxide ceramic materials. Among developers the most popular oxide materials retaining strength at high temperatures are materials based on mullite (fibrous [3, 4, 7, 8] and compact [4]); in addition, zirconium oxide is used as a functional and process additive. A typical method of synthesizing the initial powders for compact materials is presented in, for example, [9, 10]. Such compositions possess full resistance to oxidation, phase stability at high temperatures and good strength for ceramic materials [4]. However, there are many data (see, for example, [9, 10, 12]), on the proneness of compositions containing zirconium oxide to transition at high temperatures into a superplastic state.

Thus, in one of the materials developed by us and studied in [2] creep with an appreciable upper rate limit, supposedly developing by the mechanism of superplasticity, was found at temperatures 1250 – 1300°C. The evidence for this was the virtual absence of any time dependence of the flow rate, a strong dependence of the flow rate on the stress, the presence of grains on the fracture surface being pulled apart, as is characteristic for the rupture of a superplastic material, and the absence of any appreciable changes in the mechanical properties of the deformed sample. The phenomenon can be very striking in the presence of substantial porosity in the material.

A photograph of a material based on the system $Al_2O_3$–$ZrO_2$, reinforced with fibers based on mullite (CeraFib Company), after tests in a four-point bending scheme at temperature 1250°C is displayed in Fig. 1. At the indicated temperature the deformation in the sample developed so rapidly that the maximum possible rate of motion of the crossarm of the testing machine did not permit obtaining a reliably recorded response of the force sensor. This example shows that such materials must be tested for creep under a prolonged constant load at the working temperature, since often the de-

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**Fig. 1.** Sample of a material based on the system $Al_2O_3$–$ZrO_2$, reinforced with fibers based on mullite after testing at 1250°C.

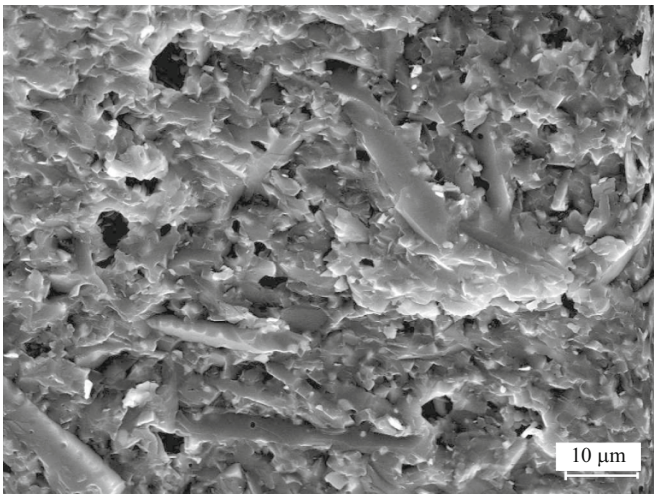


**Fig. 2.** Fracture of a ceramic sample, SEM, × 1200.

velopers optimize them to obtain the maximum short-time high-temperature strength right up to 350 – 500 and even 700 MPa, but they do not give any information on the resistance to deformation under prolonged loading.

A quantitative study of this phenomenon in materials based on the system mullite – zirconium oxide was performed by constructing a physical model of the behavior of the materials under a load.

## PROCEDURE

The phase composition of the experimental samples was determined with a DRON-3M x-ray diffractometer equipped with a computer system for recording the measurements and analyzing the results. The scans of the samples were performed in Cu radiation in the angle range $2\theta = 10 – 70°$ at points spaced by 0.05° and exposure 2 sec at each point. To identify the phases the results obtained were compared with the ASTM data tables.

As noted in [11], the physical and mechanical characteristics are the main integral quality indices for aviation structural materials. High-temperature tests with four-point bending were performed in the Instron 5882 setup equipped with a resistance furnace with molybdenum disilicide heaters, and the regular silicon carbide fittings were used. The high-temperature strength of the samples in four-point bending was determined by the procedure described in [12]. Two testing methods were used in the experiments studying the creep of the material: maintaining a constant bending load acting on a sample, while periodically fixing the movements of the crossarm as required for this, and recording the change in the values of the bending load when the position of the crossarm was recorded.

The fractures in the material were analyzed with an S-405A electron microscope with accelerating voltage 25 kV and magnification × 2000. Gold was deposited on the surface of the samples in order to drain charge. An Olympus BX-51 microscope was used for optical examination of the surface of the material in reflected light.

## EXPERIMENTAL PART

Silicon samples based on mullite modified with 10% (mass fraction) zirconium oxide, partially stabilized by yttrium oxide (3% of the mass fraction of zirconium oxide), were studied. Zirconium oxide was introduced as a sintering additive and hardener of the material at low temperatures (to 800°C). The initial powders for obtaining blanks was synthesized by the sol-gel method from zirconium and aluminum oxychlorides, yttrium chloride and silicic acid ethyl ester. The blanks were obtained by semidry bilateral pressing in a steel mold. Annealing was done in air at temperature 1670°C (the solidus point of the composition is 1710°C [13]) in 1 h. The choice of the quite high temperature and time for annealing is explained by the fact that the material was optimized to obtain the possible higher mechanical properties in the temperature range 1200 – 1350°C, including the maximum possible stability against creep under the action of long-time loads, which require a structure consisting of quite large and stable grains of the main phase (mullite). The blanks obtained were cut with a diamond disk into samples in the form of rectangular rods of width and height 3.0 – 6.25 mm and length 50 – 65 mm, which were ground with M24 corundum micropowder to remove the visible surface defects. The samples studied in the present work, in contrast to those studied previously, were subjected to long-time annealing at 1710°C for 1.5 h. This annealing was performed in order to increase the size of the grains of the main functional phase of the material (mullite), and in this way to attempt to increase the stability of the material against the development of grain-boundary creep.

X-ray phase monitoring of the material obtained as well as the study of its microstructure by means of scanning electron microscopy (SEM) (Fig. 2) showed that the material consists of a matrix comprised of mullite crystals of size 2 – 8 μm with inclusions of equiaxial particles of zirconium oxide of size 0.5 μm and smaller and reinforced with large mullite plates, up to 25 – 50 μm in length, visible in sections

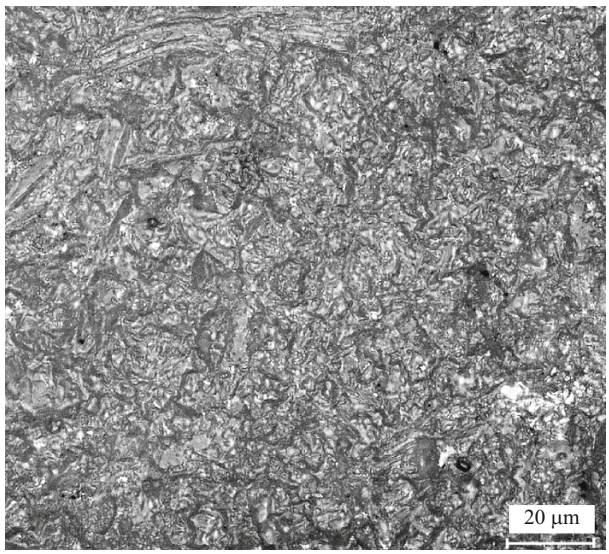


**Fig. 3.** Surface of ceramic permeated with HF, reflected light, × 750.

and fractures in the form of needles 2 – 5 μm wide and up to 50 μm long. It was noted during x-ray phase analysis that the intensity of the reflections of zirconium oxide is somewhat lower than expected, which in our opinion indicates its high dispersity and smearing over the grain boundaries of the main phase. The optical photograph (Fig. 3) of the surface of a material etched with HF also indicates the absence of a significant number of inclusions of zirconium oxide larger than 0.5 μm. Only the individual pores remaining from the $ZrO_2$ removed (the dissolution rates of mullite and zirconium oxide in HF differ by two orders of magnitude) are visible in the photograph. There were no qualitative differences in the structure of the material from those that we observed in [2], which shows that its structure is close to an equilibrium one.

It should be noted that the limited life and high cost of the equipment of the high-temperature testing machine made it necessary to limit the soaking time of the samples at high temperature under a load to times no longer than 120 – 140 min.

## RESULTS

The tests were conducted at the nominal stress, equal to 90 MPa, in the sample. The stress was picked on the basis of the fact that it must be higher than the yield stress determined in [2], but at the same time significantly lower than the short-time strength of the material.

All samples tested under a constant load at high temperature underwent slow deformation. In addition, for tests with duration 1 h the time dependence of the deformation was practically linear to within the accuracy of the results obtained. The steps formed by measurements on the displacement scale are associated with the discreteness of the apparatus (the crossarm on this setup moves in steps of 0.005 mm).

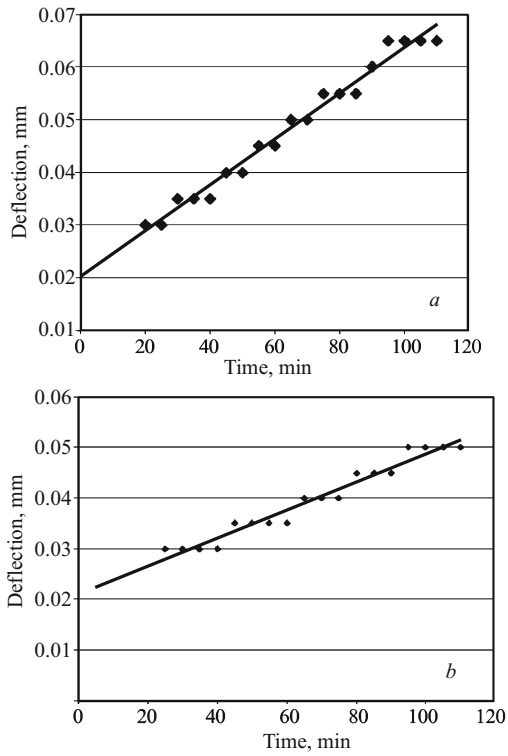


**Fig. 4.** Deformation of the samples (deflection) of ceramic versus time: *a*) 1250°C and *b* ) 1200°C.

It is evident from the data presented in Table 1 on the deformation rate of the samples and the examples shown in Fig. 4 of the dependences of the displacements on the testing time that the creep rates for different samples at constant temperature are practically constant, but they change considerably with temperature. The difference in the value of the deformation at the point '0th minute', just as its difference from zero, is related with the instability of the additive and the temperature deformations of the testing fittings during heating and the sampling of the gaps in the machine during loading. The small fluctuations of the deflection rate are associated with the difference of the transverse sizes and, in consequence, the moments of inertia of the test samples. These differences will be taken into account at the time the

**TABLE 1.** Deformation Rate of Material Under a Load

| Experiment | Test temperature, °C | Deformation rate, $10^{-6}$ m/min | Stress maintained in the sample, MPa |
|---|---|---|---|
| 1 | 1250 | 0.42 | 88 – 90 |
| 2 | 1250 | 0.43 | 88 – 90 |
| 3 | 1250 | 0.42 | 88 – 90 |
| 4 | 1200 | 0.30 | 88 – 90 |
| 5 | 1200 | 0.29 | 88 – 90 |
| 6 | 1200 | 0.29 | 88 – 90 |

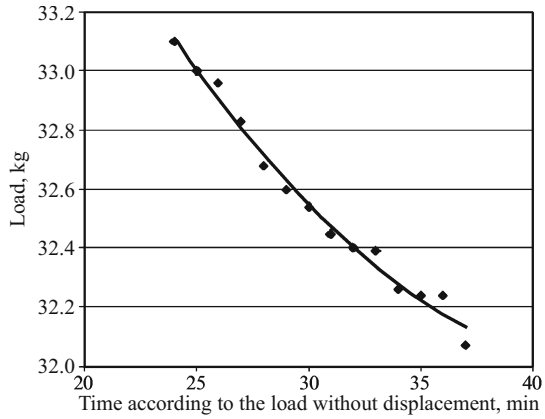


**Fig. 5.** Bending force acting on a sample versus the time with constant deformation at temperature 1200°C.

results are analyzed in subsequent phases of this work. Work to determine the relaxation rate of the stresses during the flow of the material was also started and the change in the stress in time with constant deformation of the material was measured. The magnitude of the deformation was determined because there was need to find a sample in the zone of flow development during the entire experiment. The results obtained in the process of this experiment are presented in Fig. 5.

A preliminary analysis shows that the relaxation rate of the stress in the experimental material decreases with decreasing stress, according to a preliminary estimate, almost proportionately. However, the quite low rate of creep of the tested material and the large cross section of the sample made it impossible, in our opinion, to obtain data sufficient for making a correct determination of the time dependence of the stress. Considering the limitations of the apparatus on the duration of the experiment, the problem will be solved at the next phase of this work (by performing an additional series of experiments using samples with much smaller moment of resistance of the cross section).

## CONCLUSIONS AND RECOMMENDATIONS

Data were obtained on the behavior of the recrystallized material mullite – zirconium dioxide under prolonged action of a mechanical load at high temperature. It is evident in the dependences of the displacements on the testing time that the creep rates for different samples at constant temperature are practically constant, but they change significantly with temperature. The relaxation rate of the stresses during creep was determined from the change in the stress as a function of time at constant deformation of the material. A preliminary analysis showed that the relaxation rate of the stresses in the experimental material decreases with decreasing stress according to a relation that is close to a direct proportionality.

The data obtained on the deformation of the material under a load showed quite good reproducibility of the mechanical properties and are suitable for subsequent analysis to determine the activation energy of the flow process in a material. Subsequent investigations of stress relaxation and internal friction will make it possible to construct a physical model of the mechanical properties of a material. In so doing, the stress relaxation and internal friction taking account of the properties of the material will be studied on samples with a diminished cross section.

It was determined that a material subjected to additional recrystallization annealing during the mechanical tests exhibited properties that are qualitatively identical to those of VMK-4 type material tested in [2], but the creep rate is appreciably lower. This allows us to conclude that the formation of the large-crystalline structure of the main phase appreciably improves the high-temperature mechanical properties and that quite prolonged heating of similar materials to temperatures slightly below the solidus temperature does not result in loss of performance. The data obtained also suggest that ultrafine-grain ceramic materials, which have been rapidly developed to obtain record values of the strength at moderate temperatures and short-time tests, are of no interest for use with high-temperature heating.

*Financial support for this research was provided by RFFI as part of the scientific project No. 13-08-12110-ofi_m.*

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